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EFFECTS OF THE CORONA DISCHARGE ON PETROLEUM

BY

J. J. JAKOSKY

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EFFECTS OF THE CORONA DISCHARGE ON PETROLEUM

By J. J. Jakosky

INTRODUCTION

This paper discusses experiments made to determine the effects that high-voltage alternating-current electricity in the form of the corona discharge has on petroleum vapors. It supplements Technical Paper 351,[1] which discusses tests of the effects of electric arcs on petroleum and the production of carbon black. The work described in the two papers is a part of that undertaken by the Bureau of Mines in the effort to increase efficiency in the utilization of petroleum.

During the early days of the petroleum industry the question of an adequate supply of gasoline did not arise. Before 1910 the chief petroleum products were illuminating and lubricating oils; light distillates, gas oils, and fuel oils were by-products. When the internal-combustion engine was developed, however, and particularly when the automobile industry began to expand, gasoline assumed new importance, and the necessity of obtaining a larger proportion of motor fuel from the available supply of crude oil became evident.

During the past 10 years automotive engineers have improved the internal-combustion engine and its accessories so that a fuel of lower volatility can be used successfully, thus allowing oil refiners to market a larger percentage of the crude oil as motor gasoline. This increased yield has been augmented by the supply of light gasoline obtained from natural gas and to some extent by benzol from coal. However, there have been several times in the past few years, notably in the summers of 1918 and 1920, when the consumption of motor fuel threatened to overtake production, and when there would unquestionably have been serious shortages if it had not been for the application of "cracking." Electrical discharges, properly applied, increase the rate at which the thermal cracking of petroleum proceeds.

[1] Jakosky, J. J., The Electrical Manufacture of Carbon Black: Tech. Paper 351, Bureau of Mines, 1924, 42 pp.

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CRACKING OF HYDROCARBONS

When complex hydrocarbons are strongly heated, they break down or "crack" to form hydrocarbons of simpler molecular structure. "Cracking" is widely used to make gasoline from gas oil and other heavy oils. Gasoline is the main product, but fixed gas, free carbon, and small quantities of other by-products are also formed. Some of the cracked gasoline first produced was unstable; when stored for a short time it developed a yellow or brown color and a disagreeable odor, and much of it deposited gummy and resinous substances. Consequently, it seemed to be an inferior motor fuel. These difficulties have been overcome, first, by carefully selecting the temperatures and pressures most suitable for obtaining a good yield of satisfactory gasoline, and second, by devising appropriate chemical treatment of raw gasoline to eliminate the objectionable characteristics.

COLOR IN GASOLINE

It is often assumed that "water-white" gasoline is a better fuel than a gasoline of yellowish or brownish tinge. If high-grade crude petroleum is available, water-white gasoline can easily be made by distillation and simple chemical treatment or filtration. Some grades of natural-gas gasoline, however, as well as the naphtha made from low-grade crudes, contain colored compounds which can only be removed with difficulty. The presence of colored compounds is also characteristic of most cracked gasoline unless it has been specially treated.

The removal of these colored compounds, which exist in such small percentages that they are probably harmless, entails the removal of large quantities of unsaturated hydrocarbons which are excellent motor fuels. The ideal method of treatment would remove from the cracked distillate only the least stable compounds, leaving most of the unsaturated hydrocarbons and, if necessary, part of the colored compounds in the resulting motor fuel.

CRACKED AND STRAIGHT-RUN GASOLINE

One of the outstanding differences between "cracked" and "straight-run" gasoline is the presence of unsaturated hydrocarbons in the cracked product. Many inventors and engineers have assumed, therefore, that these unsaturated hydrocarbons are responsible for the color, odor, and gummy material referred to above. More recent investigations[2] seem to indicate that this is not entirely true, and

[2] Smith, N. A. C., and Cooke, M. B., Gum-Forming Constituents in Gasoline: Reports of Investigations, Bureau of Mines, Serial 2394, September, 1922, 12 pp.

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that most unsaturated hydrocarbons are in themselves harmless. Many experimenters have tried, however, to find some way of cracking oils without forming unsaturates, and have often assumed that conditions could be found in which the unsaturated hydrocarbons could be hydrogenated or saturated by means of hydrogen or natural gas as fast as they were formed in the cracking still. The use of chemical catalysts, such as aluminum chloride, iron chloride, and iron oxide, has been studied and many patents have been issued. The effect of electric discharges on the formation of gasoline has also been studied by inventors, and some of them have concluded that under proper conditions such discharges actually prevent the formation of unsaturated hydrocarbons. The literature on the subject of hydrogenation is voluminous, and good résumés have been given by Ellis and Meigs,[3] and by Leslie.[4]

SCOPE OF REPORT

The experiments described in this paper are divided into five sections: (1) Hydrogenation using commercial compressed hydrogen gas and natural gas; (2) polymerization of benzene by the corona; (3) cracking petroleum by using a high-voltage corona discharge; (4) precipitation of hot-oil vapors; and (5) cracking by the corona without external heating. Because conditions prevailing in these experiments differ, the apparatus, procedure, and results obtained are given separately under each division. A general summary follows all of the tests and the discussion of results therefrom.

ACKNOWLEDGMENTS

The writer is greatly indebted to the following persons for help and suggestions during the course of the investigations: N. A. C. Smith, M. B. Cooke, and W. A. Jacobs, of the petroleum division of the Bureau of Mines, and F. B. Tough and E. W. Dean, formerly with the division; D. A. Lyon; A. C. Fieldner, M. W. von Bernewitz, C. M. Bouton, J. D. Davis, S. H. Katz, and R. L. Brown, of the Pittsburgh experiment station; and F. G. Cottrell, of the National Research Council and the Fixed Nitrogen Research Laboratory.

APPARATUS USED IN ALL EXPERIMENTS

Figure 1 shows the electrical equipment used in these experiments. The impedance coil, control panel, and measuring meters are at the left; the power and high-voltage transformers are on the floor; and

[3] Ellis, C., and Meigs, J. V., Gasoline and Other Motor Fuels. New York, 1921, 708 pp.
[4] Leslie, E. H., Motor Fuels, Their Production and Technology. New York, 1923, 680 pp.

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the condensers, rotary spark gap, and variable inductances are on the table.

LOW-FREQUENCY EQUIPMENT

The low-frequency electrical apparatus, shown diagrammatically in Figure 2, consisted essentially of the following: A 440 to 220 to 110-volt, 15-kv. a. distributed shell-type, step-down transformer connected to the 440-volt 60-cycle power supply. A 3-contact rotary switch was used, whereby 110, 220, or 440 volts could be supplied the primary circuit of the step-up transformer. The transformer was a rectangular close-core, low-magnetic leakage type requiring an external reactance. The reactance, in connection with the 3-contact rotary switch with taps to the primary of the transformer, allowed good control of the secondary voltage. Any electromotive force up to about 150,000 volts, 60 cycle, was available at the transformer secondary.

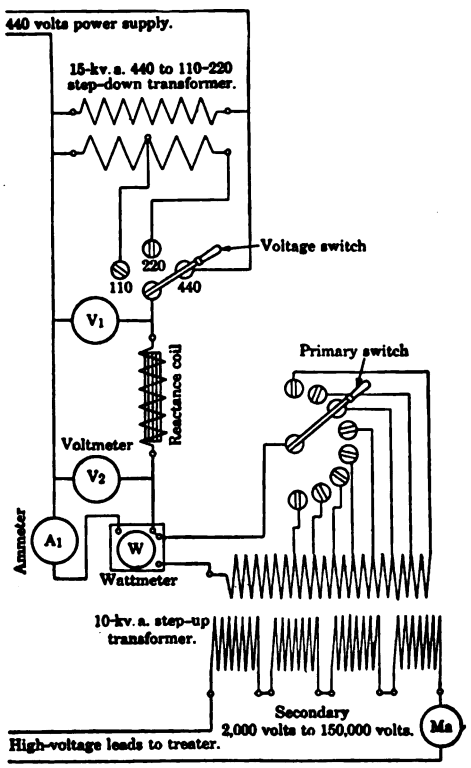

FIGURE 2.—Low-frequency electrical equipment

In the experiments on the effects of low-frequency discharges, one terminal of the secondary was connected to the central discharge wire of the treating tube, while the other terminal was connected to the tube or surrounding jacket and grounded.

HIGH-FREQUENCY SET

For the high-frequency investigations the conventional Tesla apparatus shown in Figures 3 and 4 was used. A high-voltage pyrex glass-jar condenser of variable capacity was immersed in oil and connected directly across the terminals of the transformer. In series with the condenser terminals was the primary of the Tesla resonator and a motor-driven rotary zinc-disk spark-gap. The Tesla coil is a simple air-core transformer, which in these investigations had a ratio of approximately 100 to 1 between secondary and primary. The primary was wound outside the secondary and placed at the lower end. The lower primary and secondary terminals were

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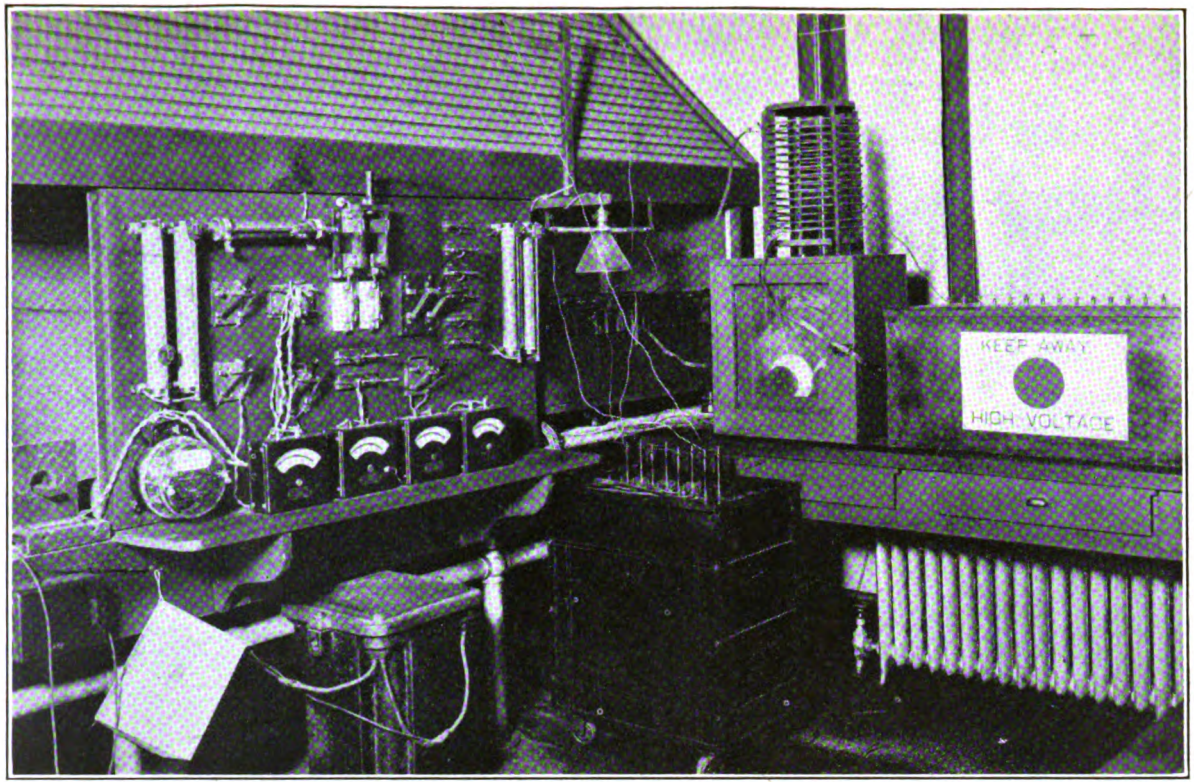

FIGURE 1.—SIXTY-CYCLE AND HIGH-FREQUENCY ELECTRICAL EQUIPMENT USED IN HYDROGENATION EXPERIMENTS

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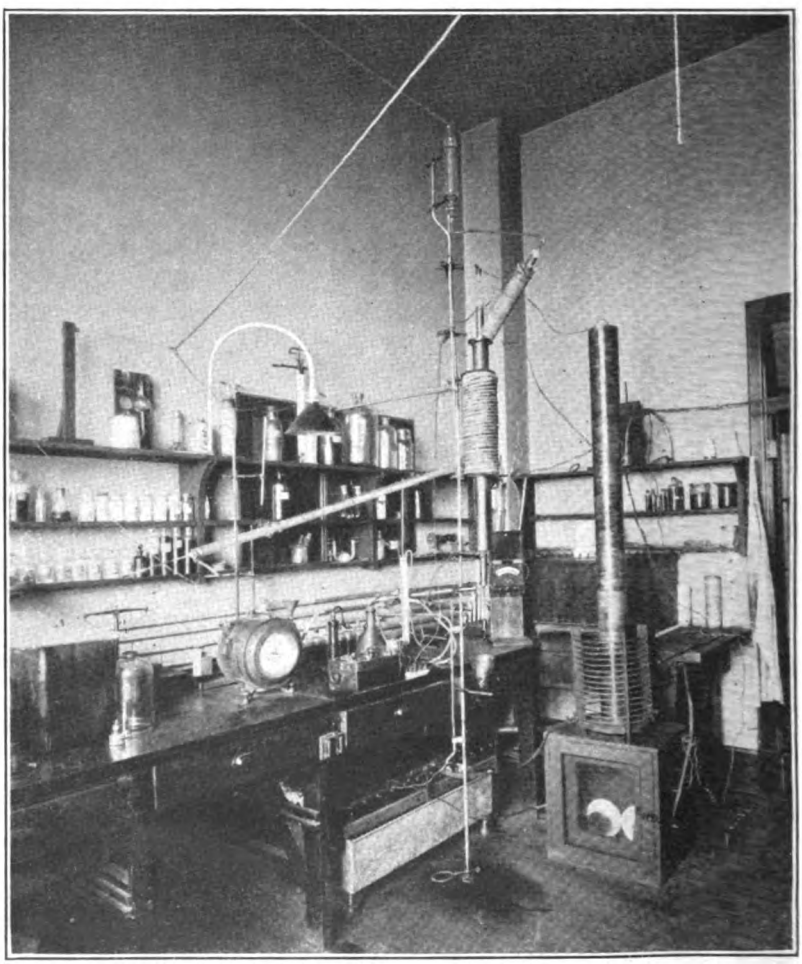

FIGURE 3.—CRACKING TUBE AND HIGH-FREQUENCY APPARATUS

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grounded to minimize high-potential, high-frequency discharges between primary and secondary, and kick-backs into the power circuits. The upper terminal of the secondary was connected to the central electrode of the treater.

The high-voltage 60-cycle current from the step-up transformer charged the condenser until the voltage across the rotary gap broke it down. The condenser then discharged through the gap, producing a high-frequency oscillatory current in the primary winding of the Tesla coil. The oscillating current in the primary induces a high-frequency electromotive force in the secondary by transformer action.

The frequency supplied the treaters used in the different experiments was varied by changing the capacity of the condenser or by varying the inductance by changing the number of turns in the primary of the Tesla coil. The frequency was calculated from the

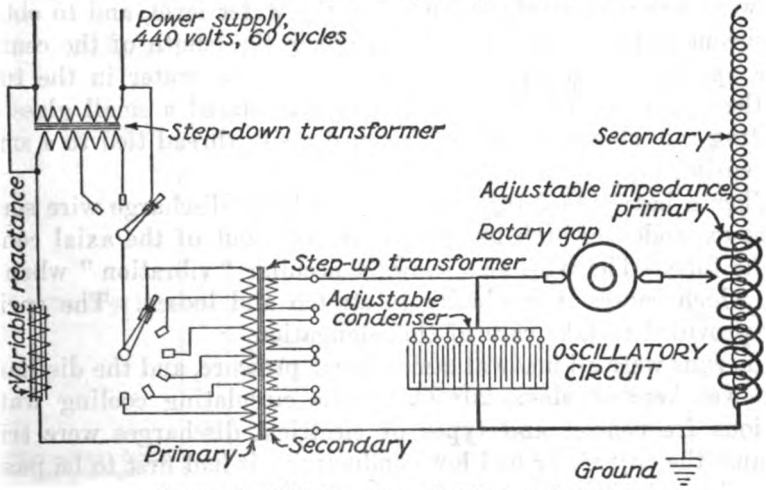

FIGURE 4.—High-frequency electrical equipment

wave-length readings obtained through the use of a conventional resonance-indicating calibrated radio wave meter; the following approximate equation was used:

$$f=\frac{300,000,000}{w}$$

where f=frequency in cycles per second; w=wave-length, in meters; and 300,000,000=a constant, velocity of electromagnetic wave propagation.

SECTION 1. HYDROGENATION EXPERIMENTS

EXPERIMENTS WITH HYDROGEN AND NATURAL GAS

Two series of experiments were made to determine whether hydrogen or natural gas could be activated for use in the hydrogenation of cracked gasoline. Unsaturated hydrocarbons are soluble in sul-

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phuric acid, consequently a considerable percentage of cracked gasoline is wasted by modern refining processes. If these compounds could be hydrogenated, this loss would be prevented.

The hydrogen used for these hydrogenation experiments was tank-compressed hydrogen such as is used for welding and other industrial purposes. It was purified by the system suggested by Wendt and Landauer.[5]

CORONA TUBE AND AUXILIARY APPARATUS

The corona tube and auxiliary apparatus are shown diagrammatically in Figure 5. The length of the discharge tube, as regards electrical effects, was varied by the height of the water in the annular space between the two tubes and the length of the central wire. When a high-frequency current is used the discharge from the wire was considerable even above the water level, and to obtain consistent results it was necessary to keep the length of the central wire approximately equal to the height of the water in the tube. At the upper end of the central wire was placed a small glass insulating rod, above which was fastened a silk thread tied to a small coil spring.

When a heavy discharge was employed, the discharge wire sometimes expanded enough to cause it to shift out of the axial center of the tube. The wire also shows a peculiar "vibration" when in use, which causes it gradually to stretch and loosen. The spring was provided to take care of this elongation.

The runs were all made at atmospheric pressure, and the discharge tube was kept at about 20° C. by the circulating cooling water. Various frequencies and types of electrical discharges were tried. Because the city water had low conductivity it had first to be passed through a soluable salt to render it sufficiently conducting to ground the system.

TEST PROCEDURE AND RESULTS OF HYDROGEN ACTIVATION

The hydrogen entered the top of the corona tube after passing through the gas purifying and drying apparatus. It then passed through the corona discharge taking place between the central wire and the walls of the tube. At the bottom of the tube the hydrogen passed into a tube containing finely broken pure sulphur, where the "activated" part of the hydrogen combined with the sulphur to form H_2S.

The gas, after passing through the sulphur tube, was bubbled through an ammoniacal solution of cadmium sulphate. The amount of H_2S was determined by titration with a standard iodine solution,

[5] Wendt, G. L., and Landauer, R. S., "Triatomic hydrogen": Jour. Am. Chem. Soc., vol. 42, May, 1920, pp. 930–946.

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after the cadmium sulphide was treated with an excess of HCl. Because very small quantities of H_2S were formed it was necessary to make 6 to 15 hour runs to obtain even a noticeable precipitate.

Many runs were made in which conditions were varied. In no one of them, however, was it possible to obtain more than 0.008 per

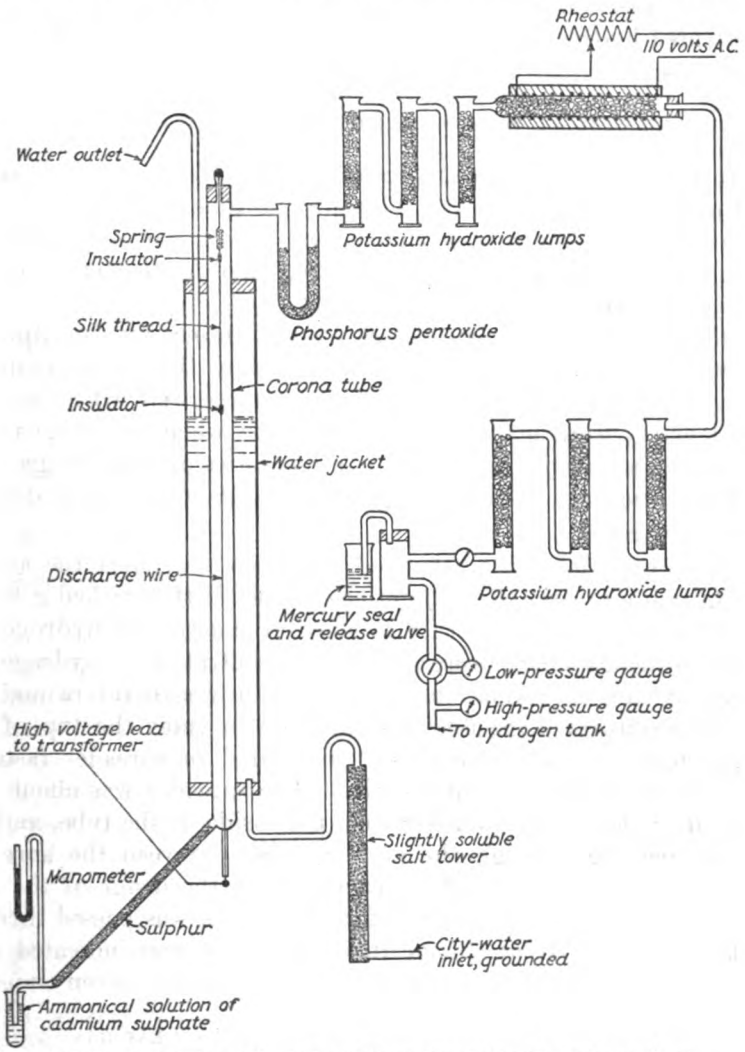

FIGURE 5.—Corona tube and auxiliary apparatus for hydrogenation

cent activation, as indicated by formation of H_2S. Attempts to determine the life of the activated hydrogen were made by varying the distance between the bottom of the discharge tube and the sulphur. At distances too great no hydrogen sulphide is formed. The maximum time during which H_3 can exist in a reactive concentration is about 40 seconds at the pressure and temperature used.

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A greater amount of activated hydrogen (H_3) is probably formed in the corona itself than is evidenced by the H_2S produced when the gas passes through the pulverized sulphur. As there should be an equilibrium between H_3 and H_2 in the corona discharge, attempts were made to study it. Results, however, were very inconsistent, and no definite relation could be found between the percentage of activated hydrogen formed and the corona current, length of discharge tube, etc.

ATTEMPTS AT HYDROGENATION OF CRACKED GASOLINE

Saturation of unsaturated (approximately 36 per cent) cracked gasoline was attempted next. The sulphur tube was replaced with a tube containing the gasoline and the activated gas bubbled through. Blank runs were made with the current off in order to correct for the effects of evaporation, etc.

In these experiments unsaturation was determined by the sulphuric acid method and was checked by determining the iodine numbers (Hanus method).[6] No differences, except those well within experimental error, were noted between the runs when the corona was discharging and when it was not. In one series of runs the gas was bubbled through the unsaturated gasoline for 18 hours, but no definite effects were noted.

Because the life of the activated hydrogen was short the author thought that a greater effect might be obtained if the cracked gasoline were present in the corona tube to absorb the activated hydrogen as fast as formed, thereby decreasing the concentration of hydrogen as H_3 and favoring its formation. The apparatus was therefore modified and the unsaturated gasoline was allowed to enter the top of the corona chamber and flow over an "umbrella" or spreader fastened to the upper end of the central wire. The spreader was about one-eighth inch smaller in diameter than the inside of the tube, and the gasoline passing through the annular space between the spreader and the tube flowed by surface tension down the inside of the tube in a thin, continuous film. As before, hydrogen was passed through the tube. No apparent change in unsaturation was indicated even after the gasoline was passed through the apparatus seven times.

ATTEMPTS AT SATURATION BY USE OF NATURAL GAS

Numerous patent disclosures state that natural gas is susceptible to activation by the corona discharge and that the polymerization of natural gas into heavier liquid hydrocarbons is possible. Conditions under which these reactions are reputed to occur vary greatly,

[6] For details of these methods, see Dean, E. W., and Hill, H. H., Determination of Unsaturated Hydrocarbons in Gasoline: Tech. Paper 181, Bureau of Mines, 1917, 25 pp.

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as specified in the different patents issued. Because of the impossibility of trying all conditions a few runs were made at atmospheric pressure and at temperatures of 20, 100, and 500° C. The same corona apparatus was used as in the hydrogenation experiments with natural gas of the following composition: CH_4, 86.1 per cent; C_2H_6, 12.1 per cent; H_2, 1.8 per cent; C_2H_4, trace; CO, trace; CO_2, none; O_2, none. The gas purifying and drying apparatus as used in the hydrogenation experiments was omitted and the gas flowed directly to the corona tube.

RESULTS WITH NATURAL GAS

The runs at 20 and 100° C. indicated that the corona discharge slowly dissociated natural gas with formation of hydrogen and free carbon. Carbon black was deposited upon the central discharge wire and there was a trace on the walls of the treater tube. The percentage of hydrogen in the treated gases increased gradually and there were no indications of polymerization or the formation of any hydrocarbons of heavier molecular weight than those in the original gas.

In the run at 500° C. (obtained by using a metal tube surrounded by an electric heater, described in more detail later) a very slight trace of tarry matter formed on the walls of the tube. This same deposit formed whether the corona was on or not and it was therefore assumed to be the result of heat and not of the corona discharge.

SECTION 2. CORONA DISCHARGE EXPERIMENTS TO DETERMINE BENZENE POLYMERIZATION

A modified apparatus was used with benzene (C_6H_6) vapor (fig. 6). It consisted essentially of a hot-water-heated, 1-inch pyrex tube 84 inches long, used as a reaction chamber, and a central discharge wire or electrode. Tap water rendered conductive by passing through a slightly soluble salt flowed into the jacket surrounding the pyrex reaction tube. The benzene used was treated previously with sulphuric acid and caustic soda, neutralized, and then distilled twice to remove any polymerized gums or heavy products. The rate of vaporization was controlled with an electric heating coil so that a gentle stream of vapor flowed from the outlet of the treater tube.

The benzene vapors passed through the corona discharge, which took place between the central wire and the walls of the container.

RESULTS OF POLYMERIZATION OF BENZENE

A light, slightly viscous, brown liquor gradually collected on the walls of the tube and drained into the collecting trap. It had an odor very similar to pinol, and upon oxidation (by bubbling ozone

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through the liquid) definite crystals formed. The odor of the resultant compound was pleasant, sharp, and penetrating, closely re-

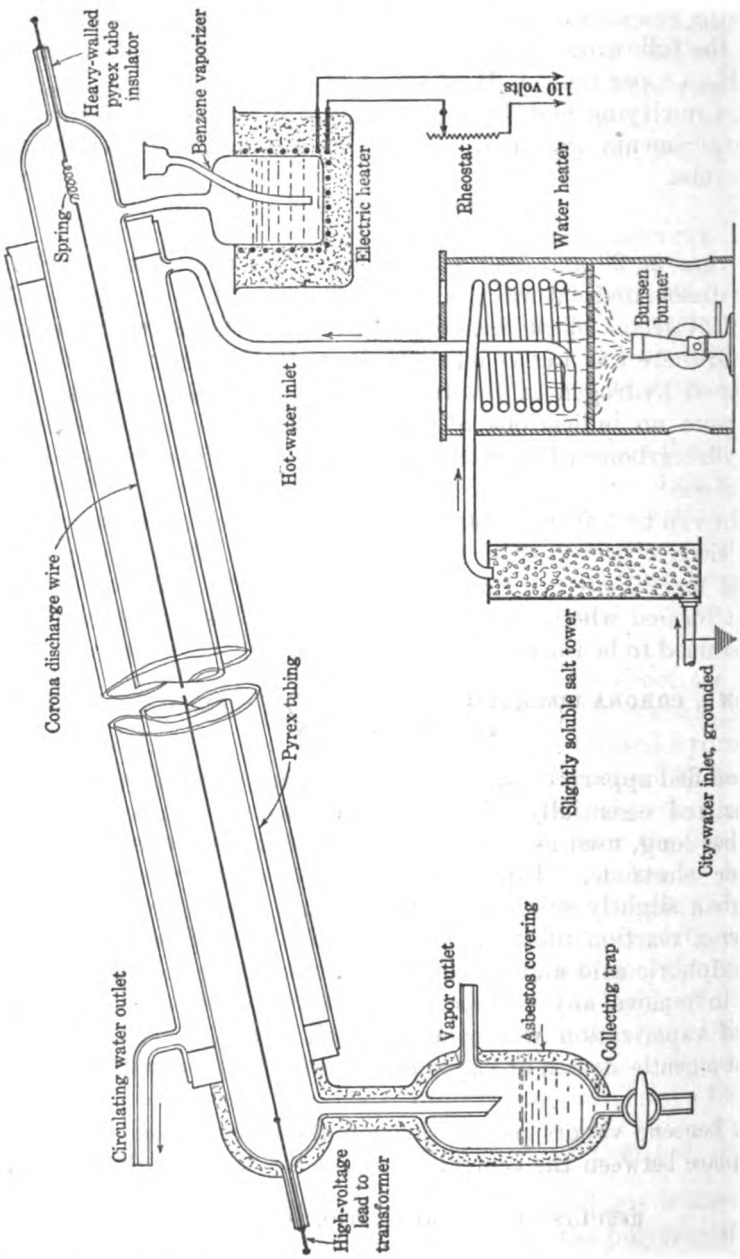

FIGURE 6.—Apparatus used in polymerization tests

sembling that of pinene, which would seem to indicate the presence of terpenes or terpene derivatives. Further investigation of the

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effect of the corona discharge on such polymerization and condensation reactions seems warranted.

SECTION 3. EXPERIMENTS IN CRACKING, USING CORONA DISCHARGES

To study the effects of electrical discharges during actual cracking the furnace shown in Figures 3 and 7 was constructed. The apparatus consisted essentially of an oil reservoir, a preheater where the oil was vaporized prior to cracking, a cracking chamber (a seamless iron tube 2 inches in diameter and 40 inches in length), a water-cooled condenser, an oil trap, an oil scrubber for removal of the light hydrocarbons, a wet meter for measuring the gas produced during the run, electric heaters for the preheater and cracking chamber, and the necessary meters and control devices.

In constructing the furnace particular care was taken to

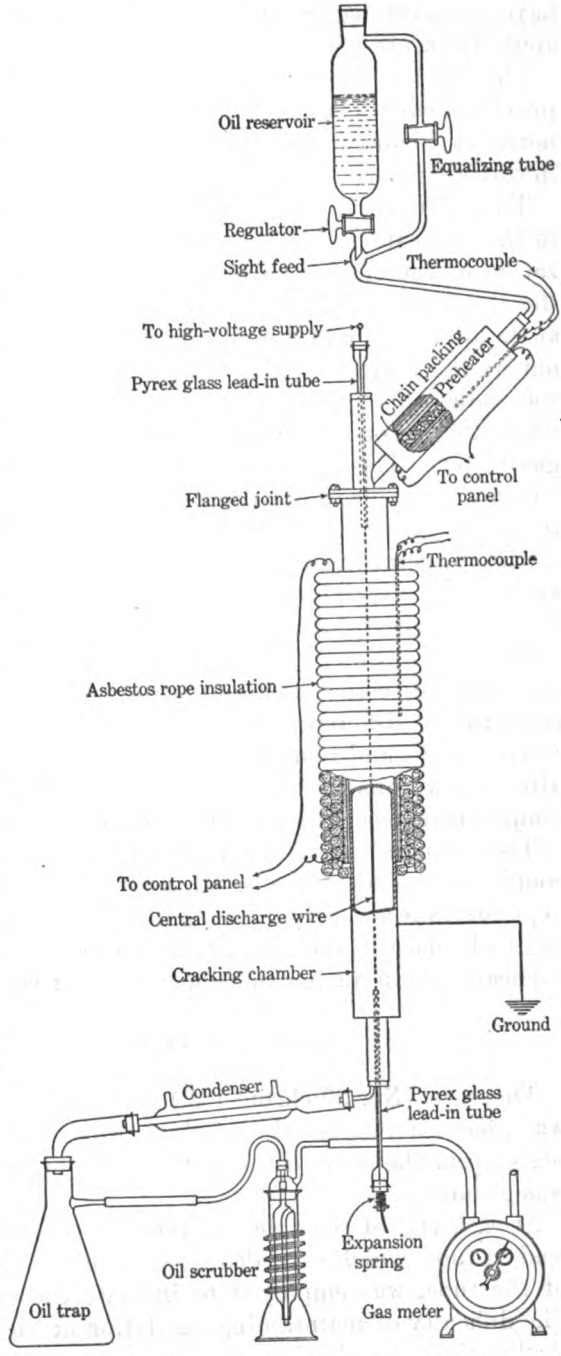

FIGURE 7.—Cracking chamber for studying effect of corona discharges during cracking

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have all joints tight, and all piping connections were made at an angle to insure efficient drainage.

The oil for the run was placed in the oil reservoir, which was provided with a stopcock and a sight-feed dropper. The flow was noted at frequent intervals and was held at the rate of 1,000 c. c. in three hours.

The oil dropped from the feed-in tube upon the chain packing in the preheater. This packing was used to obtain effective vaporization of the oil and to prevent unvaporized oil from flowing into the cracking tube. The oil vapors entered the cracking chamber at its upper end and flowed downward through the heated zone and out at the bottom of the tube into the condenser. The condensate was collected in the trap and the volatile vapors in the scrubber, while the uncondensable gases passed through the scrubber to the gas meter. The pressure of the system was maintained at about 3 inches of water to overcome the back pressure of the scrubber and the gas meter.

The temperatures in the cracking tube were measured by chromel-alumel thermocouples placed between the heaters and the iron tube. During the early experiments thermocouples were used at the top, center, and bottom of the tube. Because of the design of the furnace (the heating coil was wound closer at the ends of the tube) the temperature difference along the cracking tube was found not to exceed 10° C. and remained constant during the runs. Accordingly, after a few runs the two end thermocouples were removed and the temperature recorded was that of the center thermocouple.

The temperature of the preheater was measured with a thermocouple embedded in the metal wall of the preheater itself and was kept constant at 400° C. throughout the runs. Practically no cracking took place in the preheater, as almost no carbon formed on the preheater chain during the whole series of runs.

INSULATION OF DISCHARGE WIRE

The wire (No. 20 chromel A) from which the corona discharged was placed axially in the cracking tube; the corona discharge took place from the wire to the walls of the metal cracking tube, which was grounded.

At each end of the cracking tube a heavy-walled pyrex insulating lead-in tube, which extended about 3 inches beyond the narrow part of the tube, was employed to insulate the central discharge wire. The difficulty of maintaining insulation at high temperatures (practically all dielectrics became conductive at temperatures approaching red heat) was avoided by this construction. The lead-in tubes kept free from carbon deposits during the runs, probably because

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the heavier oils condensed on them slightly. A tension spring was provided at the bottom of the apparatus to take up any expansion of the discharge wire.

TEST PROCEDURE

To start a run the preheater and cracking-tube furnace were brought to the required temperatures by regulating the current flow in the heating coils. The oil to be cracked was then placed in the reservoir and the sight-feed dropper adjusted.

Three complete runs were conducted at each of the following temperatures: 500, 600, 700, 800, and 900° C.

The first run of each series omitted the corona discharge and the cracking was purely thermal. In the second run the pyrolytic conditions prevailing in the first run were duplicated as closely as possible and a high-frequency corona discharge was allowed to take place from the central wire to the interior wall of the tube. The vapors passing through the tube were thus subjected to the combined effects of thermal cracking and of the corona. The corona voltage was maintained as high as possible without causing arcing between the central wire and the walls of the tube. In the third run of each series a low-frequency, 60-cycle corona was used in place of the high-frequency discharge.

OIL USED

The oil used during the runs was a "gas oil" of the following characteristics:

Specific gravity	0.829
A. P. I. gravity, degrees	39.2
Unsaturation, per cent	4

Distillation analysis

FIRST DROP 146° C. BAROMETER, 733 MM.

Temperature, °C.	Per cent cut	Sum per cent	Specific gravity cut	°A. P. I. cut	Temperature, °F.
Up to 200	2.5	2.5	0.787	48.3	Up to 392
200-225	4.3	6.8			392-437
225-250	11.9	18.7	.806	44.1	437-482
250-275	16.3	35.0	.818	41.5	482-527

VACUUM DISTILLATION AT 40 MM.

Up to 200	17.3	17.3	0.830	39.0	Up to 392
200-225	23.9	41.2	.839	37.2	392-437
225-250	14.9	56.1	.848	35.4	437-482

ANALYSIS OF PRODUCTS

The oils recovered from the runs were distilled in a standard Bureau of Mines Hempel distillation outfit,[7] and the fractions that

[7] Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., The Analytical Distillation of Petroleum and Its Products: Bull. 207, Bureau of Mines, 1922, 82 pp.

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boiled below 275° C. were used for comparison. Unsaturation indicates the solubility of the oil in concentrated sulphuric acid. Because of the small quantities employed, unsaturation of the entire recovered oil was used as a basis for comparing the quality of the cracked products.

RESULTS OF CRACKING TESTS

Comparisons of the corona-free, high-frequency and low-frequency corona runs are given in Figures 8, 9, and 10. The effects of the

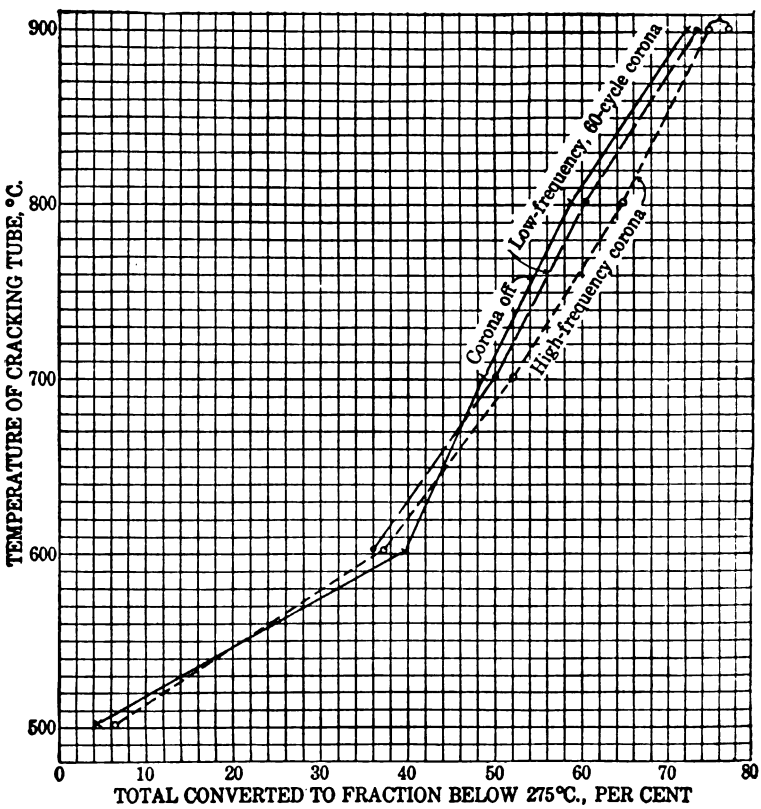

FIGURE 8.—Effects of corona discharge on conversion of gas oil to gasoline-kerosene fraction

corona are inappreciable at temperatures below 600° C. for the particular conditions prevailing during these runs.

Figure 8 shows the total percentage conversion. The lowest rate of conversion was obtained when the corona was not used, and a greater conversion was obtained with the high-frequency corona than with the low-frequency discharge.

The unsaturation of the recovered oil is also lowest without the corona and highest with the use of the high-frequency discharge. This relationship is shown graphically in Figure 9.

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Figure 10 shows the quantity (cubic feet) of noncondensable gas formed per gallon of oil treated. Generally speaking, the minimum amount of gas was formed with the corona off, and the largest volume was formed when the high-frequency corona was used.

These data indicate that the use of a corona discharge gives greater cracking than without the corona, as was attested by the higher unsaturation and larger amount of noncondensable gas formed, as well as greater yield of cracked products.

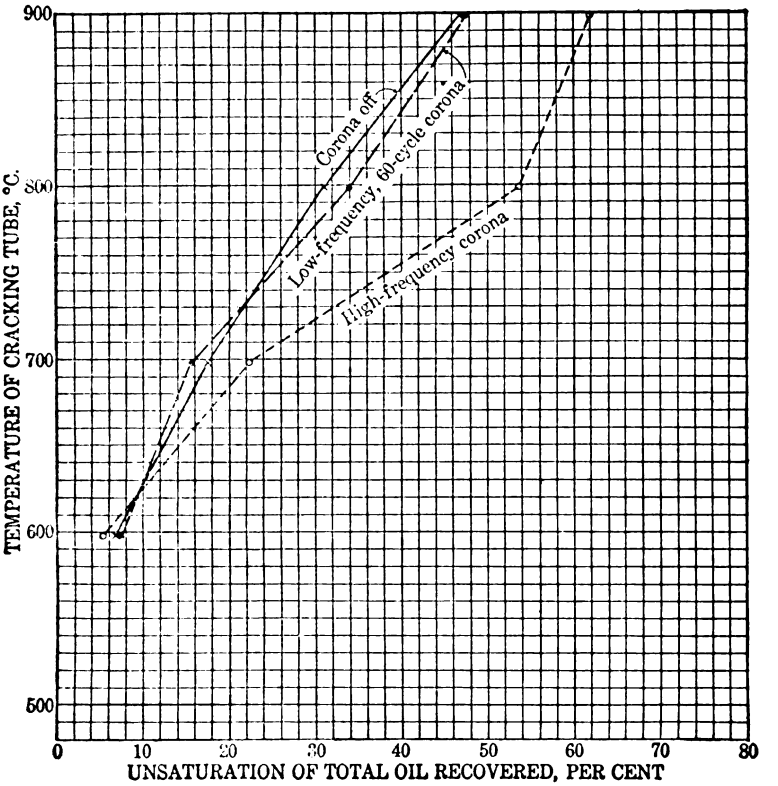

FIGURE 9.—Effects of corona discharges on unsaturation of recovered oil

SECTION 4. PRECIPITATION OF HOT OIL VAPORS

APPARATUS USED

Experiments were conducted to ascertain whether the corona itself had any mechanical effect on hydrocarbon vapors. A heavy-walled pyrex tube, 20 inches long and 1½ inches in diameter, sealed at the bottom and provided with a stopper connecting with a water-cooled condenser, was placed in a vertical position. Two separate nichrome-wire heating coils, one 6 inches high at the bottom of the tube, and

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one 12 inches long one-fourth inch above the lower coil, were placed around the tube.

The tube was filled to a height of about 5 inches with benzene (C_6H_6, boiling point 80.6° C.). The benzene was vaporized by means of the lower coil; the temperature of the vapor in the upper part of the tube was maintained at any desired value by means of the upper heater. A central discharge rod 16 inches long and one-eighth inch in diameter was placed in the tube, and when sufficient voltage was used a good corona discharge took place between the rod,

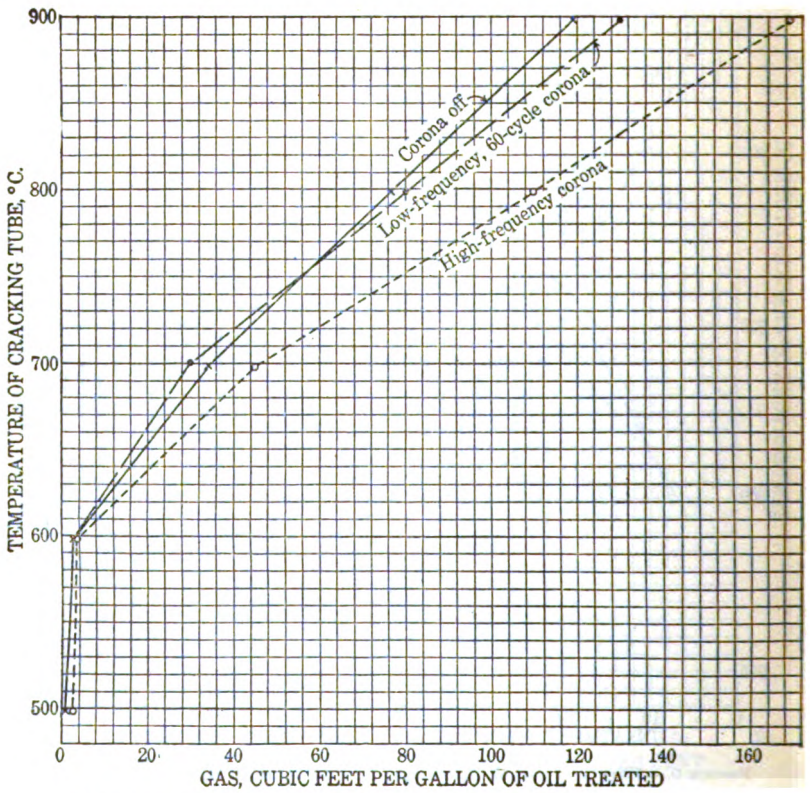

FIGURE 10.—Effects of corona discharges on gas formed during cracking

through the walls of the tube by condenser action, to the heating coils outside; one terminal of each coil was grounded.

RESULTS OF PRECIPITATION TESTS

A series of runs was made in which the temperature in the upper part of the tube was varied. It was found that when the temperature of the vapor was below a certain critical value a major part of the vapor was precipitated against the walls of the tube. If,

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however, the temperature was above this value the vapors passed out of the tube and were condensed and collected by the water-cooled condenser fastened to the top of the pyrex tube. The temperature at which this phenomenon occurred varied with the rate of flow of the vapor and to some extent with the type of discharge.

An arc light and condensing lens (photomicrograph projection equipment [8]) were next arranged to throw a beam of light into the upper part of the tube. The critical precipitating point was found to occur at approximately the temperature marking the change from a visible cloudiness or mist to an invisible gas, or the reverse. When the vapor temperature was above the critical value the vapor was practically invisible. As the temperature was decreased below this value the greater became the fog or mist within the tube. This observation was made with the corona off; starting the corona caused a momentary increase of mist, then a fairly rapid disappearance. The corona caused precipitation of the mist against the walls of the tube, and resultant reflux, or reevaporation, depending upon the wall temperature.

Above this critical temperature the oil vapor appeared to exist as a gas and was practically unaffected by the corona. Below the critical temperature part of the vapor exists as mist or minute liquid particles which are carried in suspension by the gas, and are acted upon by the corona.

Later observations on similar effects were made by J. D. Davis in his work on electrostatic precipitation of coal-tar mists, and communicated to the writer on February 28, 1922, as follows:

> In hot precipitation of low-temperature coal-tar mist by the corona discharge in the laboratory it was found that the tars were partly cracked when the tube was maintained at a temperature of 600 to 700° C., and the resultant carbon was thrown down by the precipitation. Tar mists were practically completely precipitated.

RELATIONSHIP BETWEEN VAPOR AND WALL TEMPERATURE

Dean and Jacobs,[9] in previous work on vapor-phase cracking, found that the temperature of the furnace walls is the controlling factor in cracking. They also found that the temperature of the through-going vapor may be somewhat less than the wall temperature, the amount depending upon the rate of feed, the pressure, and the diameter of the cracking tube.

The oil vapor in the center of the cracking tube is cracked less due to lower temperature and absence of the surface-contact effect.

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[8] The writer is indebted to W. M. Myers, mineralogist at the Bureau of Mines Nonmetallic Minerals station, New Brunswick, N. J., for the use of this equipment.

[9] Dean, E. W., and Jacobs, W. A., Production of Gasoline by Cracking Heavier Oils: Tech. Paper 258, Bureau of Mines, 1922, 55 pp.

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The greater the " channeling " of the vapors the lower the percentage of cracking.

SECTION 5. CRACKING DUE TO THE CORONA

Attempts were made to crack in the vapor phase by using the corona without heating the cracking tube higher than the temperature required to vaporize the oil. The original apparatus shown in Figure 7 was used and the temperature of the lower heating coil was maintained the same as the preheater.

A gas oil was used, and the analysis of the original oil and the treated oil, which had been run through the apparatus 10 times, showed only a very slight cracking, which probably was largely due to the small amount of cracking that took place during the vaporization of the gas oil in the preheating chamber and treating tube. Only a small trace of carbon was deposited on the central discharge wire and none on the walls of the tube.

CONCLUSIONS

Much interest has been manifested during recent years in the use of the corona discharge during the cracking of petroleum to increase the production of gasoline. It is known that ionization may be caused by high voltages as well as by purely thermal means and that apparently some relationship exists between electrical and thermal activation. By means of electrical activation some chemical reactions may be made to proceed at temperatures lower than when thermal activation alone is employed. The chemical effects, however, even when a very high-voltage corona is used, are of small magnitude and in keeping with the comparatively small amount of energy which may be applied by using the corona.

In the polymerization of benzene previously mentioned, however, the corona effect is of major importance. Although it is theoretically possible that benzene may be polymerized by high temperatures, the product formed would probably be unstable at such temperatures and would decompose.

Claims have been made that the use of a high-frequency discharge would, by its high frequency, cause some molecular rearrangement and vibrations of the molecules and electrons that would bring about chemical changes. When it is considered, however, that the frequency of vibrations of the electrons and atoms composing a molecule is many thousands of times greater than that of the high-frequency current, chemical changes from the effects of any high-frequency current seem improbable. The smaller amount of cracking obtained by the use of the 60-cycle current, as compared to the high-frequency current (figs. 8, 9, and 10), is probably due to the

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lower voltages at low frequencies which had to be used to prevent breaking down the corona into an arc.

The corona discharge probably has two effects when used during the cracking of oils—a chemical action and a mechanical or precipitating action. There is, undoubtedly, some direct chemical effect due to the use of the corona. Many investigators [10] have studied both low and high frequency discharges on different gases and vapors, and in virtually every case the investigators have reported some effects. The effect is, however, comparatively slight and in keeping with the relatively small amount of energy of the corona. The mechanical or precipating effect may be important.

The writer [11] found in another investigation that a high-frequency discharge or arc did not decompose natural gas. His apparatus consisted essentially of two spaced electrodes and an inlet tube for bringing the natural gas in contact with the arc. When a 60-cycle arc (either high or low voltage) was used, the gas was partly decomposed into its elements, hydrogen and carbon. If, however, a high-frequency discharge was used, no decomposition (as evidenced by carbon liberated) occurred. The high-frequency arc was obtained by shunting an adjustable high-voltage condenser directly across the electrodes without any additional inductance in the circuit. The arc was very hot, and as measured by an optical pyrometer was hotter than the low-frequency (60-cycle) arc. These experiments seem to indicate that the decomposition of natural gas by the electric arc is not purely a thermal effect or heat reaction.

PROBABLE FUNCTION OF THE CORONA IN THERMAL CRACKING

The increased cracking obtained by the use of the corona during the thermal cracking of oil appears to be due: (1) To precipitation of the hot oil vapors or mist particles against the walls of the cracking tube; and (2) to the decreased amount of channeling by the "electric wind" set up by the corona discharge. The effects are due largely to a purely mechanical or "precipitation" effect of the corona discharge on the droplets and particles in the field between the corona discharge wire and the walls of the tube. Tolman and

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[10] Tesla, Nikola, Corona Chemical Effects: U. S. Patent 568177, Sept. 22, 1896.
Shenstone, W. A., and Priest, Martin, "Studies on the formation of ozone from oxygen": Jour. Chem. Soc., vol. 63, 1893, pp. 938–961.
Rideal, E. K., Ozone. New York, 1920, pp. 109–107.
Anderegg, F. O., "A chemical study of the high-frequency corona discharge": Proc. Indiana Acad. Sci., 1921.
Schmidt, W. A., and Wolcott, E. R., Cracking Petroleum by Aid of Electric Discharges: U. S. Patent 1307931, June 24, 1919.
Kaufmann, H. P., ["Products of the action of the silent electric discharge on acetylene"]: Ann., Bd. 417, 1918, pp. 34–59; Chem. Abs., vol. 13, 1919, p. 1925.

[11] Jakosky, J. J., The Electrical Manufacture of Carbon Black: Tech. Paper 351, Bureau of Mines, 1924, p. 20.

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Karrer[12] have shown that the motion of droplets and particles in the field of a corona discharge is due to their obtaining an electric charge by one of four different methods: (1) By electrostatic induction; (2) by conduction from the earth when the jet is grounded; (3) by absorption of gaseous ions present in the field of the corona discharge; (4) by direct contact with the central wire.

PROBABLE APPLICATION OF MIST PRECIPITATION

In cracking petroleum, compounds of many different molecular weights and boiling points are present in the cracking tube. The lighter, more volatile constituents exist as gases at the cracking-tube temperature. The heavier hydrocarbons, however, exist as vapor or mist. The gases are unaffected by the corona, whereas the vapor or mist particles are precipitated against the hot walls of the cracking tube by the corona discharge, and increased cracking results. Although the increased cracking obtained when the corona was used in these experiments was only 5 to 8 per cent, it is possible that a higher percentage would be obtained in larger cracking tubes. The data indicate that the greater the tendency of the gas to "channel" the greater should be the effect of the corona.

Because the physical properties of compounds in the form of gases or mists differ, the effect of the corona is selective. This action[13] suggests its use in the exit line of a cracking still to prevent the heavier fractions from being carried along by the cracked gasoline (existing as a gas at the cracking-tube temperature) into the dephlegmators and condensers. In this way the corona would serve three useful functions: (1) Reduce the load on the condensing system; (2) increase the over-all thermal efficiency of the plant by preventing the loss of the heat of the condensation and reevaporation of heavy hydrocarbons; (3) increase the thermal efficiency of the still by keeping the heavy hydrocarbons continually in it.

SELECTIVE CONDENSATION BY USE OF THE CORONA

The corona precipitator may also be used in special knockdown boxes or tubes and fractional condensers; also in increasing the efficiency of condensers by preventing or minimizing channeling of the through-going vapors. Such applications would be similar to present uses of the electrostatic precipitator in many industries, especially acid-mist precipitation in sulphuric acid and similar plants.

[12] Tolman, R. C., and Karrer, Sebastian, "Motion of droplets and particles in the field of the corona discharge": Chem. and Met. Eng., vol. 22, June 30, 1920, pp. 1203–1206.

[13] Complete patent applications covering utilization of the phenomena have been filed by the author.

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SUMMARY

The results of these investigations may be summarized thus:

1. Electrical activation of hydrogen, as well as the use of hydrogen or natural gas for the hydrogenation of unsaturated cracked gasoline by the use of the corona discharge, is of such small magnitude as to be negligible in the refining of petroleum and production of gasoline.

2. Benzene was polymerized by use of the corona discharge. Suggestions are made and attention is called to the importance of further work in this direction.

3. The use of a corona discharge in a vapor-phase cracking furnace is shown to give an increased degree of cracking, as indicated by recovered products, gas yield, and unsaturation. The use of a high-frequency corona gave a greater percentage of cracking than the 60-cycle discharge.

4. The work showed that a critical temperature existed below which an oil vapor existed as a mist, was visible in a strong beam of light, and could be precipitated by a corona discharge.

Previous work by Bureau of Mines investigators indicated that the furnace wall had a higher temperature than the through-going vapors, and the degree of cracking depended upon the "surface-contact" effect.

5. The corona discharge in itself produced no cracking of the gas oil present in the vapor phase.

(*a*) Dissociation of natural gas by the electric arc is not purely a thermal reaction process.

(*b*) These results indicate that the increased cracking obtained with the use of a corona is due to a mechanical precipitation of the heavier oil particles or mist against the hot walls of the cracking tube.

(*c*) Possible applications of the use of the corona discharge in petroleum practice are discussed and uses suggested for knockdown boxes or tubes, fractional condensers, dephlegmators, and run-back lines are given.

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